# Physical and Chemical Hydrogeology

## Second Edition

## Patrick A. Domenico

David B. Harris Professor of Geology Texas A&M University

## Franklin W. Schwartz

Obio Eminent Scholar in Hydrogeology The Obio State University



John Wiley & Sons, Inc.

New York Chichester Weinheim Brisbane Toronto Singapore

# **Contents**

# Chapter 1 Introduction 1

#### 1.1 What Is Hydrogeology? 1

Physical Hydrogeology Before the Early 1940s 2 Chemical Hydrogeology Before the Early 1960s 3 Post-1960 Hydrogeology 4

# 1.2 The Relationship Between Hydrogeology and Other Fields of Geology 4

#### 1.3 Hydrologic Cycle 5

Components of the Hydrologic Cycle 5 Evapotranspiration and Potential Evapotranspiration 7 Infiltration and Recharge 8 Base Flow 8 Hydrologic Equation 10

## Chapter 2

#### The Origin of Porosity and Permeability 13

#### 2.1 Porosity and Permeability 13

Porosity and Effective Porosity 13 Permeability 15

#### 2.2 Continental Environments 16

Weathering 16

Erosion, Transportation, and Deposition 17

Fluvial Deposits 17
Eolian Deposits 20
Lacustrine Deposits 20
Glacial Deposits 20

#### 2.3 The Boundary Between Continental and Marine Environments 20

#### 2.4 Marine Environments 21

Lateral and Vertical Succession of Strata 21 Ancestral Seas and Their Deposits 22

The Paleozoic Rock Group 23 The Mesozoic Rock Group 24

The Cenozoic Rock Group 24

Diagenesis in Marine Environments 24

Porosity Reduction: Compaction and Pressure Solution 24

Chemical Rock-Water Interactions: Secondary Porosity in Sandstones 26

#### 2.5 Uplift, Diagenesis, and Erosion 27

The Style of Formations Associated with Uplift 27 Secondary Porosity Enhancement in Carbonate Rocks 29

## 2.6 Tectonism and the Formation of Fractures 29

Style of Fracturing 30 Fluid Pressure and Porosity 31 Connectivity 31

# Chapter 3 Ground-Water Movement 33

## 3.1 Darcy's Experimental Law and Field Extensions 33

The Nature of Darcy's Velocity 34 Hydraulic Head: Hubbert's Force Potential 34 The Gradient and Ground-Water Flow 36 Physical Interpretation of Darcy's Proportionality Constant 36 Units and Dimensions 37

## 3.2 Hydraulic Conductivity and Permeability of Geologic Materials 37

Observed Range in Hydraulic Conductivity
Values 37
Character of Hydraulic Conductivity
Distribution 38
Anisotropicity and Heterogeneity Within
Units 39
Heterogeneity Among Units and the Classification
of Aquifers 41
Creating Hydraulic Conductivity Averages 42
Darcy's Law for Anisotropic Material 43
Measurement of Hydraulic Conductivity 44
Laboratory Testing 44

The Search for Empirical Correlations 44

- 3.3 Mapping Flow in Geological Systems 45
  Hydrogeological Cross Sections 46
  Potentiometric Surface and Water-Table Maps 47
  Closing Statements 48
- 3.4 Flow in Fractured Rocks 48

  Continuum Approach to Fluid Flow 48

  Intergranular Porous Rocks 49

  Fractured Rocks 49
- 3.5 Flow in the Unsaturated Zone 51
  Hydraulic and Pressure Heads 51
  Water Retention Curves 53
  Darcy's Law for Variably Saturated Flow 54
  Unsaturated Flow in Fractured Rocks 54

# Chapter 4 Main Equations of Flow, Boundary Conditions, and Flow Nets 58

- 4.1 Organizing the Study of Ground-Water Flow Equations 58
- **4.2 Conservation of Fluid Mass 59**Main Equations of Flow 60
- 4.3 The Storage Properties of Porous Media 62
  Compressibility of Water and Its Relation to
  Specific Storage for Confined Aquifers 63
  Compressibility of the Rock Matrix: Effective
  Stress Concept 64
  Matrix Compressibility and Its Relation to
  Specific Storage of Confined Aquifers 65
  Equation for Confined Flow in an Aquifer 67
  Specific Yield of Aquifers 68
- **4.4 Boundary Conditions and Flow Nets 68**Graphic Flow Net Construction 71
- 4.5 Dimensional Analysis 72

# Chapter 5 Ground Water in the Basin Hydrologic Cycle 75

5.1 Topographic Driving Forces 75The Early Field Studies 75Conceptual, Graphical, and Mathematical Models of Unconfined Flow 76

Effects of Basin Geometry on Ground-Water Flow 78

Effects of Basin Geology on Ground-Water Flow 80 Ground Water in Mountainous Terrain 83 Ground Water in Carbonate Terrain 87 Ground Water in Coastal Regions 88 The Fresh Water-Salt Water Interface in Coastal Regions 89

The Ghyben-Herzberg Relation 89
The Shape of the Interface with a Submerged Seepage Surface 90
Upconing of the Interface Caused by Pumping Wells 91

- 5.2 Surface Features of Ground-Water Flow 91
   Recharge-Discharge Relations 91
   Ground Water-Lake Interactions 93
   Ground Water-Surface Water Interactions 95
- 5.3 Some Engineering and Geologic Implications of Topographic Drive Systems 97
  Large Reservoir Impoundments 97
  Excavations: Inflows and Stability 98
  The Sea-Level Canal 98
  Ground-Water Inflows into Excavations 99
  The Stability of Excavations in Ground-Water Discharge Areas 99
  Landslides and Slope Stability 101

# Chapter 6 Hydraulic Testing: Models, Methods, and Applications 103

- 6.1 Prototype Geologic Models in Hydraulic Testing 103
- 6.2 Conventional Hydraulic Test Procedures and Analysis 105

The Theis Nonequilibrium Pumping Test Method 105

The Curve-Matching Procedure 107 Assumptions and Interpretations 107 Modifications of the Nonequilibrium Equation 108

Time-Drawdown Method 108
Distance-Drawndown Method 109
Steady-State Behavior as a Terminal Case of the
Transient Case 109
The Heatish Joseph Lealer Agrifus Method 110

The Hantush-Jacob Leaky Aquifer Method 110 Water Table Aquifers 112

- 6.3 Single-Borehole Tests 114
  Recovery in a Pumped Well 114
  The Drill Stem Test 114
  Slug Injection or Withdrawal Tests 115
  Response at the Pumped Well: Specific Capacity
- 6.4 Partial Penetration, Superposition, and Bounded Aquifers 118
  Partial Penetration 118
  Principle of Superposition 118
  Bounded Aquifers 120

and Well Efficiency 116

- 6.5 Hydraulic Testing in Fractured or Low-Permeability Rocks 122 Single-Borehole Tests 123 Multiple-Borehole Tests 123
- 6.6 Some Applications to Hydraulic Problems 124

Screen Diameter and Pumping Rates 125 Well Yield: The Step-Drawdown Test 125 A Problem in Dewatering 125 A Problem in Water Supply 127

#### 6.7 Computer-Based Calculations 128

Code Demonstration 131 Bounded Aguifers Revisited 131

## Chapter 7

#### Ground Water as a Resource 136

#### 7.1 Development of Ground-Water Resources 136

The Response of Aquifers to Pumping 136 Yield Analysis 137

Case Study: The Upper Los Angeles River Area 137

Management Strategies 139

Artificial Recharge 139

Conjunctive Use 141

#### 7.2 Introduction to Ground-Water Flow Simulation 142

Generalized Modeling Approach 142 Conceptual Model 142 Ground-Water Flow Simulation 143 Evaluation of Model Results 144 Model Verification 144

A Note of Caution 144

#### 7.3 Formulating a Finite-Difference Equation for Flow 145

Description of the Finite-Difference Grid 145 Derivation of the Finite-Difference Equation 146

#### 7.4 The MODFLOW Family of Codes 147

Solving Systems of Finite-Difference Equations 148 Modular Program Structure 148 Illustrative Example 148 Operational Issues 152 Time-Step Size 152 Drawdowns at "Pumping" Nodes 152 Water-Table Conditions 153

7.5 Case Study in the Application of MODFLOW 154

**Boundary Conditions 153** 

Model Development 154 Data Preparation and Model Calibration 156

## Chapter 8

#### Stress, Strain, and Pore Fluids 159

#### 8.1 Deformable Porous Media 159

One-Dimensional Consolidation 159

Three-Dimensional Consolidation 169

Development of the Flow Equation 159

The Undrained Response of Water Levels to Natural Loading Events 160

The Drained Response of Water Levels to Natural Loading Events 163

Land Subsidence as a One-Dimensional Drained Response 163

Mathematical Treatment of Land Subsidence 165

Elastic Properties in Deformational Problems 169 Flow Equations for Deformable Media 171

#### 8.2 Abnormal Fluid Pressures in Active **Depositional Environments 172**

Origin and Distribution 172

Mathematical Formulation of the Problem 174 Isothermal Basin Loading and Tectonic Strain 175

One-Dimensional Basin Loading 176 Extensions of the One-Dimensional Loading Model 177

Thermal Expansion of Fluids 179 Fluid Pressures and Rock Fracture 182 Phase Transformations 183 Subnormal Pressure 184 Irreversible Processes 185

#### 8.3 Pore Fluids in Tectonic Processes 185

Fluid Pressures and Thrust Faulting 185 Seismicity Induced by Fluid Injection 186 Seismicity Induced in the Vicinity of Reservoirs 187 Seismicity and Pore Fluids at Midcrustal Depths 188 The Phreatic Seismograph: Earthquakes and Dilatancy Models 188

#### Chapter 9

#### Heat Transport in Ground-Water Flow 191

#### 9.1 Conduction, Convection, and Equations of **Heat Transport 191**

Fourier's Law 192 Convective Transport 193 Equations of Energy Transport 194 The Heat Conduction Equation 195 The Conductive-Convective Equation 195 **Dimensionless Groups** 196

#### 9.2 Forced Convection 197

Temperature Profiles and Ground-Water Velocity 197 Heat Transport in Regional Ground-Water Flow 199 Heat Transport in Active Depositional **Environments 203** Heat Transport in Mountainous Terrain 205

#### 9.3 Free Convection 207

The Onset of Free Convection 207 Sloping Layers 208 Geological Implications 208

9.4 Energy Resources 209

Geothermal Energy 209 Energy Storage in Aquifers 209

#### 9.5 Heat Transport and Geologic Repositories for Nuclear Waste Storage 210

The Nuclear Waste Program 210 The Rock Types 210 Thermohydrochemical Effects 212 Thermomechanical Effects 213

Chapter 10		
Solute	Transport	215

#### **10.1 Advection 215**

#### 10.2 Basic Concepts of Dispersion 216 Diffusion 218 Mechanical Dispersion 219

#### 10.3 Character of the Dispersion Coefficient 220

Studies at the Microscopic Scale 220 Dispersivity as a Medium Property 221 Studies at Macroscopic and Larger Scales 221

#### 10.4 A Fickian Model of Dispersion 223

#### 10.5 Mixing in Fractured Media 226

#### 10.6 A Geostatistical Model of Dispersion 228 Mean and Variance 228 Autocovariance and Autocorrelation Functions 229 Generation of Correlated Random Fields 230

#### 10.7 Tracers and Tracer Tests 231

Estimation of Dispersivity 230

Field Tracer Experiments 232 Natural Gradient Test 232 Single Well Pulse Test 232 Two-Well Tracer Test 233 Single Well Injection or Withdrawal with Multiple Observation Wells 233 Estimates from Contaminant Plumes and

**Environmental Tracers 233** Massively Instrumented Field Tracer Tests 233 Borden Tracer Experiment 234 Validation of the Stochastic Model of Dispersion 235

#### Chapter 11 Principles of Aqueous Geochemistry 238

#### 11.1 Introduction to Aqueous Systems 238 Concentration Scales 239 Gas and Solid Phases 240

#### 11.2 Structure of Water and the Occurrence of Mass in Water 240

#### 11.3 Equilibrium Versus Kinetic Descriptions of Reactions 240 Reaction Rates 241

#### 11.4 Equilibrium Models of Reaction 241 Activity Models 242

## 11.5 Deviations from Equilibrium 243

- 11.6 Kinetic Reactions 244
- 11.7 Organic Compounds 245

#### 11.8 Ground-Water Composition 248 The Routine Water Analysis 248 Specialized Analyses 249

#### 11.9 Describing Chemical Data 250 Abundance or Relative Abundance 252 Abundance and Patterns of Change 253

#### Chapter 12 Chemical Reactions 255

#### 12.1 Acid-Base Reactions 255

Natural Weak Acid-Base Systems 256 CO<sub>2</sub>-Water System 256 Alkalinity 257

#### 12.2 Solution, Exsolution, Volatilization, and Precipitation 258

Gas Solution and Exsolution 258 Solution of Organic Solutes in Water 258 Volatilization 259 Dissolution and Precipitation of Solids 262 Solid Solubility 262

#### **Complexation Reactions 263** Stability of Complexes and Speciation Modeling 263

Major Ion Complexation and Equilibrium Calculations 264 Enhancing the Mobility of Metals 265 Organic Complexation 265

#### 12.4 Reactions on Surfaces 266

Sorption Isotherms 266 Hydrophobic Sorption of Organic Compounds 267  $K_d$ -based Approaches for Modeling the Sorption of Metals 269 Multiparameter Equilibrium Models 269

Biotransformation of Organic Compounds 276

#### 12.5 Oxidation-Reduction Reactions 272 Oxidation Numbers, Half-Reactions, Electron Activity, and Redox Potential 272 Kinetics and Dominant Couples 275 Control on the Mobility of Metals 276

#### 12.6 Hydrolysis 277

#### 12.7 **Isotopic Processes 277** Radioactive Decay 277 **Isotopic Reactions 278** Deuterium and Oxygen-18 279

#### Chapter 13 Colloids and Microorganisms 282

#### 13.1 A Conceptual Model of Colloidal Transport 282

Occurrence of Colloidal Material 283 Stabilization 283 Transport and Filtration 284

#### Colloidal Transport in Ground Water 284 Sampling and Measuring 284

Studies at Cape Cod 285

#### 13.3 Microbiological Systems 285

Biofilms 287 Sampling and Enumerating Microbial Populations 287 Plate Counts 288

### 13.4 Microbial Processes 291

Issues in Biodegradation 292 Biofilm Kinetics 292

#### 13.5 Biotransformation of Common Contaminants 293

Hydrocarbons and Derivatives 293 Halogenated Aliphatic Compounds 294 Halogenated Aromatic Compounds 294 Polychlorinated Biphenyls (PCBs) 295 Complex Transformation Pathways 295

#### Chapter 14 The Equations of Mass Transport 296

#### 14.1 Mass Transport Equations 296

The Diffusion Equation 296 The Advection-Diffusion Equation 297 The Advection-Dispersion Equation 297

#### 14.2 Mass Transport with Reaction 298 First-Order Kinetic Reactions 298

Equilibrium Sorption Reactions 299 Heterogeneous Kinetic Reactions 299

#### 14.3 Boundary and Initial Conditions 300

#### Chapter 15 Mass Transport in Natural Ground-Water Systems 303

#### 15.1 Mixing as an Agent for Chemical Change 303

The Mixing of Meteoric and Original Formation Waters 303 Diffusion in Deep Sedimentary **Environments 305** 

#### 15.2 Chemical Reactions in the Unsaturated **Zone 306**

Gas Dissolution and Redistribution 306 Weak Acid-Strong Base Reactions 307 Sulfide Oxidation 309 Gypsum Precipitation and Dissolution 309 Cation Exchange 309 Organic Reactions 309

#### 15.3 Chemical Reactions in the Saturated **Zone 310**

Weak Acid-Strong Base Reactions 310 Dissolution of Soluble Salts 312 **Redox Reactions 312** Cation Exchange 315

#### 15.4 Case Study of the Milk River Aquifer 316

#### 15.5 Age Dating of Ground Water 319

Direct Methods 319 Tritium 319

Carbon-14 320 Chlorine-36 322 **Indirect Methods 322**  $\delta^{18}$ O and  $\delta$ D 322 Chlorofluorocarbons 322

#### Chapter 16 Mass Transport in Ground-Water Flow: Geologic Systems 326

#### 16.1 Mass Transport in Carbonate Rocks 326 The Approach Toward Chemical Equilibrium in

Carbonate Sediments 327 The Problem of Undersaturation 329

Dolomitization 330

#### 16.2 Economic Mineralization 330

Origin of Ore Deposits 331 Roll-Front Uranium Deposits 331 Mississippi Valley-Type Lead-Zinc Deposits 332 Noncommercial Mineralization: Saline Soils and Evaporites 337

#### 16.3 Migration and Entrapment of **Hydrocarbons 337**

Displacement and Entrapment 337 Basin Migration Models 339

#### 16.4 Self-Organization in Hydrogeologic Systems 341

Patterning Associated with Dissolution 341 Patterning Associated with Precipitation and Mixed Phenomena 341

#### Chapter 17 Introduction to Contaminant Hydrogeology 344

#### 17.1 Sources of Ground-Water Contamination 344

Radioactive Contaminants 346 Trace Metals 347 Nutrients 349 Other Inorganic Species 349 Organic Contaminants 349

Petroleum Hydrocarbons and Derivatives 349 Halogenated Aliphatic Compounds 350 Halogenated Aromatic Compounds 350 Polychlorinated Biphenyls 350 Health Effects 350 **Biological Contaminants 350** 

#### 17.2 Solute Plumes as a Manifestation of Processes 352

Fractured and Karst Systems 357 Babylon, New York, Case Study 357 Alkali Lake, Oregon, Case Study 359

#### 17.3 Design and Quality Assurance Issues in Solute Sampling 360

Design of Sampling Networks 360 Assuring the Quality of Chemical Data 362

#### 17.4 Sampling Methods 362

Conventional Wells or Piezometers 362 Multilevel Samplers 363 Solid and Fluid Sampling 364 Cone Penetrometry 365 Other Sampling Methods 367 Dissolved Contaminants in the Unsaturated Zone 367

## 17.5 Indirect Methods for Detecting Contamination 367

Soil-Gas Characterization 367 Geophysical Methods 368 Electrical Methods 369 Ground-Penetrating Radar 370 Magnetometry 371 Seismic Methods 371

#### Chapter 18 Modeling the Transport of Dissolved Contaminants 372

#### 18.1 Analytical Approaches 372

Advection and Longitudinal Dispersion 372
The Retardation Equation 375
Radioactive Decay, Biodegradation, and
Hydrolysis 376
Transverse Dispersion 377
Models for Multidimensional Transport 378
Continuous Sources 378
Numerical Integration of an Analytical
Solution 380
The Instantaneous Point Source Model 380

# 18.2 Programming the Analytical Solutions for Computers 382

## 18.3 Numerical Approaches 384

A Generalized Modeling Approach 384 The Common Solution Techniques 385 Adding Chemical Reactions 386

## 18.4 Case Study in the Application of a Numerical Model 386

#### Chapter 19 Multiphase Fluid Systems 393

#### 19.1 Basic Concepts 393

Saturation and Wettability 393 Interfacial Tension and Capillary Forces 394 Imbibition and Drainage 394 Relative Permeability 395 Solubility and Effective Solubility 397

#### 19.2 LNAPLs and DNAPLs 398

Conceptual Models for the Occurrence of LNAPLs 399 Occurrence of DNAPLs in Ground Water 401 Secondary Contamination Due to NAPLs 401 Conceptual Models and Quantitative Methods 403 A Case Study of Gasoline Leakage 404 Hyde Park Landfill Case Study 404

#### 19.3 Partitioning 405

# 19.4 Fate of Organics in the Unsaturated Zone 406

Volatilization 406
Gas Transport by Diffusion 408
Equilibrium Calculations of Mass
Distributions 409

Mass of VOC in Gas Phase 411 Mass of VOC in Aqueous Phase 411 Mass of VOC in Sorbed Phase 411 Mass of VOC in NAPL Phase 411

# **19.5 Fate of Organics in the Saturated Zone 411** Equilibrium Calculations of Mass

Distribution 412

### 19.6 Air-Permeability Testing 412

# 19.7 Recognizing DNAPL Sites 413 Systematic Screening Procedure 414

#### Chapter 20 Remediation: Overview and Removal Options 417

#### 20.1 Containment 417

Slurry Walls 417
Sheet Pile Walls 418
Grouting 418
Surface Seals and Surface Drainage 418
Hydrodynamic Controls 419
Stabilization and Solidification 420

#### 20.2 Management Options 420

#### 20.3 Overview of Methods for Contaminant Removal 420

Excavation and Ex Situ Treatment 421 Pump and Treat 421 Interceptor Systems 421 Soil-Vapor Extraction 421

#### 20.4 Pump and Treat 422

The Problem of Pump and Treat 422 Technical Considerations with Injection-Recovery Systems 423 Methods for Designing Pump-and-Treat Systems 425

Expanding Pilot-Scale Systems 425 Capture Zones 426 Analytical Approaches to Defining Capture Zones 426 Model-Based Approaches for the Design of Recovery Systems 429 Simulation-Optimization Techniques 429 Issues in the Design of Capture Zones 430

#### 20.5 Interceptor Systems for NAPL Recovery 430

## 20.6 Soil-Vapor Extraction 431

Components of an SVE System 432

- When Can SVE Systems Be Used? 433
  Estimating Removal Rates 434
  Removal Rate Calculations 435
  Field Estimates of Soil Permeability 435
  Heterogeneity and the Efficiency of SVE
  Systems 436
- 20.7 Air Sparging 437
  Airflow and Channeling 437
  Designing Air-Sparging Systems 438
- 20.8 Case Studies in Site Remediation 438
  Oil Spill: Calgary, Alberta 438
  Gilson Road: Nashua, New Hampshire 439
  Hyde Park Landfill: Niagara Falls, New York 440
  Groveland Wells Site, Massachusetts 441

#### Chapter 21 In Situ Destruction and Risk Assessment 443

- 21.1 Intrinsic Bioremediation 443
- 21.2 Bioventing and Bioslurping 445
  Applicability of the Technology to Contaminant
  Groups 446
  Requirements for Success with Bioventing
  Systems 446
  In Situ Respiration Testing 447
  Progress in Solvent Bioremediation 448

- 21.3 Abiotic Chemical Destruction 449
  Reactive Barrier Systems 450
  Funnel-and-Gate Systems 450
- 21.4 Risk Assessment 450
  Data Collection and Data Evaluation 451
  Exposure Assessment 451
  Toxicity Assessment 453
  Health-Risk Assessment 454
  Types of Risk Assessments 455
  Environmental Risk Assessment 456
- 21.5 Fernald Case Study 456
  Detailed Risk Assessment 457

#### Answers to Problems 461

Appendix A
Derivation of the Flow Equation in a
Deforming Medium 463

Appendix B
About the Computer Disk 464

Appendix C Table of Atomic Weights 466

References 468

Index 494